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# Guidelines for Preventing Sulfidation Corrosion Failures in Chevron Refining: Comparison of API RP 939-C and Chevron Practice

# Rev. 0

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**Scope: Compare Chevron practices to an upcoming industry document and help set guidelines for the Chevron Refining effort to avoid sulfidation failures.**

This document serves to summarize and clarify the information contained in a draft industry document, API RP 939-C, for use within the Chevron Refining system to help guide the effort to avoid sulfidation failures. It is not meant to fully capture all of the available information. We will issue an update to this document when RP 939-C is published.

**Introduction: High temperature operation has the potential to lead to sulfidation and "blow-out" failures; discussion of hydrogen-free sulfidation and $H_2/H_2S$ corrosion.**

Repeated sulfidation corrosion failures in the refining industry prompted the industry to draft a recommended practice, API RP 939-C "Guidelines for Avoiding Sulfidation Corrosion Failures in Oil Refineries[1]". Sulfidation corrosion occurs in equipment that processes sulfur-containing hydrocarbon streams operating at temperatures above approximately 450°F. Sulfidation corrosion typically leads to general or uniform thinning of piping and equipment. Therefore, failures of refinery equipment due to sulfidation can often have severe consequences such as ruptures, blow-outs, and fires. Examples of such blow-out failures are shown in Figures 1 and 2.

Two sulfidation mechanisms are widely recognized; sulfidation occurring with hydrogen and sulfidation occurring without the presence of hydrogen. Hydrogen-free sulfidation, which includes processes where hydrogen is not intentionally added to the process stream, occurs in the presence of sulfur compounds at temperatures above approximately 450°F in carbon steel. Typical units subject to hydrogen-free sulfidation include the crude/vacuum unit, FCC, and coker. Sulfidation corrosion that occurs in the presence of hydrogen, such as in hydroprocessing units, is often referred to as $H_2/H_2S$ corrosion. Carbon steel can be subject to sulfidation corrosion at temperatures above

450°F in the presence of hydrogen. The mitigation strategies for each mechanism are different and will be discussed in more detail in Revision 1 of this document.

**Similarities between API 939-C and Chevron's guidelines: Agreement on the fundamentals of sulfidation corrosion**

The basics of sulfidation are generally well understood and there is a large amount of agreement between the draft API document and Chevron's thinking on the topic. The similarities between the information presented in API 939-C and Chevron's understanding include the following:

- Temperature is the most important factor in determining whether or not sulfidation will occur in a given system. For hydrogen-free sulfidation with a given temperature and sulfur content, increasing the Cr content of the steel from carbon steel to 5Cr and 9Cr will decrease corrosion rates. The 300 series stainless steels are virtually immune to sulfidation.
- There are significant differences between hydrogen-free sulfidation and $H_2/H_2S$ corrosion. Unlike hydrogen-free sulfidation, where increasing the Cr content of the steel to 5Cr or 9Cr will decrease corrosion rates for a given temperature, $H_2/H_2S$ corrosion requires upgrading to 300 series stainless steel to obtain any significant resistance.
- The sulfur content of the stream also plays a primary role in determining sulfidation rates, with higher sulfur contents leading to increased corrosion rates. However, the relationship is not as definitive as the temperature effect and the various sulfur compounds present in crude oil each have a different effect on sulfidation corrosion rates.
- Silicon content of carbon steel plays a large role in the likelihood of sulfidation occurring. Carbon steels containing low levels of silicon (Si <0.10 wt. %) are at a greater risk of sulfidation compared to those with higher silicon contents.
- The hydroprocessing distillation section adds complexity to predicting sulfidation. While technically there is little or no hydrogen in the distillation

section, corrosion rates are often similar to those experienced in the presence of hydrogen. For this reason, hydroprocessing distillation sections are considered separately from both hydrogen-free sulfidation and $H_2/H_2S$ corrosion.

- There are several secondary factors that need to be understood when considering the likelihood of sulfidation. These include the nature of the hydrocarbon phase, flow velocity, and the presence of coke. These secondary variables are more fully described in the API document.

**Differences between the API 939-C guidance and Chevron's guidelines: Chevron's method to predict $H_2/H_2S$ corrosion and hydrogen-free sulfidation corrosion rates**

While the basics of sulfidation are agreed upon, there are certain points, specifically relating to the prediction of corrosion rates, where Chevron's guidance diverges from the guidance presented in API 939-C. The differences stem from the fact that there is tremendous scatter in the available sulfidation corrosion rate data and actual rates are difficult to predict. The differences between API 939-C and Chevron's guidelines include:

- Chevron maintains a set of proprietary curves to determine $H_2/H_2S$ corrosion rates. We believe these curves are more accurate in determining corrosion rates than the industry-standard Couper-Gorman curves included in API 939-C. While the current thinking is that these Chevron $H_2/H_2S$ curves may be slightly conservative, they should be used for determining sulfidation rates in the presence of hydrogen. The proprietary Chevron curves are included in Appendix A of this report, along with an embedded spreadsheet to calculate corrosion rates based on temperature, $H_2S$ partial pressure, and material of construction.
- To be conservative and within the industry guidance, Chevron recommends the use of the API 581[2] tables to determine hydrogen-free sulfidation corrosion rates. The information from these tables is shown in graphical form in Appendix B for carbon steel, 5Cr, and 9Cr. However, there are two caveats to

using the API 581 data to determine corrosion rates; the data does not differentiate between crude unit and hydroprocessing distillation section sulfidation corrosion rates and the data is possibly over-conservative in most circumstances. Chevron is currently working on a multi-year project to prevent sulfidation failures. As part of this work, we would like to try to lead an industry effort to more accurately predict hydrogen-free sulfidation corrosion rates. In the meantime, we recommend the API 581 tables for predicting hydrogen-free sulfidation corrosion rates.

**Guidelines for New Construction: Materials of construction for high-temperature service**

For new equipment, API 939-C and Chevron recommend the following materials of construction:

- Hydrogen-free service, 2 wt. % sulfur:
  - Fully-killed (Si> 0.10 wt. %) carbon steel up to temperatures of 525°F
  - 5Cr – 0.5Mo for temperatures between 525°F and 620°F*
  - 9Cr – 1Mo for temperatures greater than 620°F**
  - 300 series stainless steels to virtually eliminate sulfidation corrosion
- $H_2/H_2S$ service:
  - 300 series stainless steel above 500°F

**Guidelines for Existing Equipment: Remediation recommendations for existing equipment at risk of sulfidation**

Chevron agrees with the guidelines presented in API 939-C for avoiding sulfidation corrosion failures in existing equipment. The API document outlines suitable

* Past Chevron guidance allowed for a 150°F "credit" for the use of 5Cr, but we now believe this may be too liberal due to variations in the Cr content of 5Cr materials.

** Although the API guidance gives "no limit" for 9Cr, Chevron would carefully review any 9Cr piping operating above 750°F.

inspection techniques for detecting sulfidation corrosion and gives guidance on corrosion monitoring and corrosion inhibitor usage.

Chevron's draft mitigation strategies are in agreement with the API guidelines while providing additional details for at-risk systems. The draft mitigation strategies are broken down into three levels of severity (low, medium, and high) based on temperature for three classes of units (crude/FCC/coker, hydroprocessing units exclusive of the distillation section, and the hydroprocessing distillation section). Each level of severity will have an action plan associated with it. ETC will seek feedback and endorsement on this mitigation plan from the Refining system. These strategies will then be included in a future version of this document, to be published once API 939-C has been published.

**Summary and Future Work**

- We are currently in the process of identifying where we there is a risk of sulfidation failures in our Refining system.
- ETC has developed a proposed mitigation strategy for at-risk systems and will soon ask for comments and endorsement of this strategy, while at the same time addressing specific cases of at-risk equipment.
- ETC will update this document with a "Revision 1" to include the mitigation strategy after API 939-C is published.
- Longer term, Chevron will work with others in the industry to try to more accurately predict sulfidation corrosion rates.

**References**

[1] "Guidelines for Avoiding Sulfidation Corrosion Failures in Oil Refineries," API RP 939-C. Pending publication.

[2] "Risk-Based Inspection Resource Document," API Publication 581. First edition, May 2000.


**Figure 1** Hydrogen-free sulfidation corrosion failure of NPS 8 piping. The relatively uniform thinning resulted in a sizable rupture. (Image courtesy of ConocoPhillips, reproduced courtesy of the American Petroleum Institute).

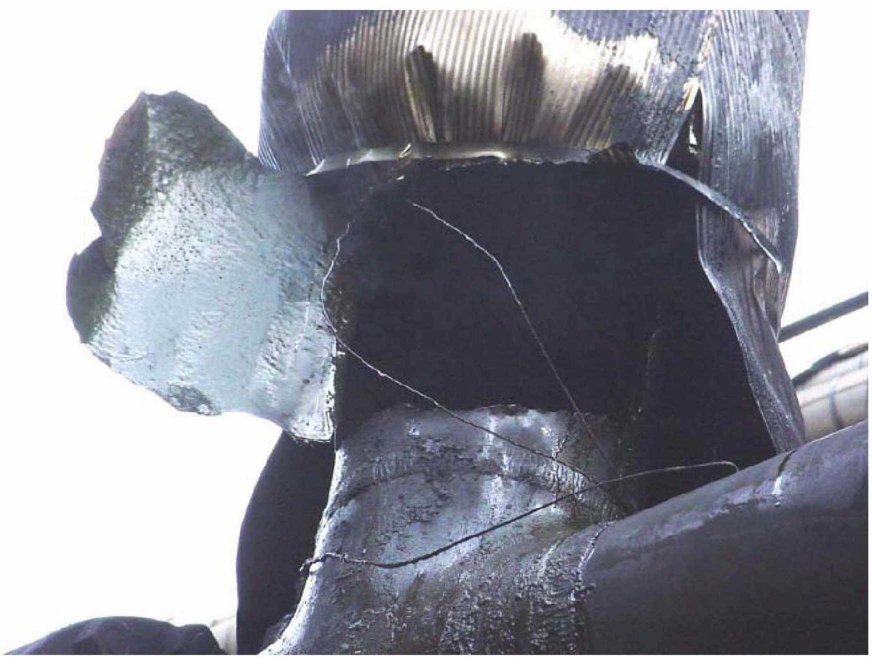
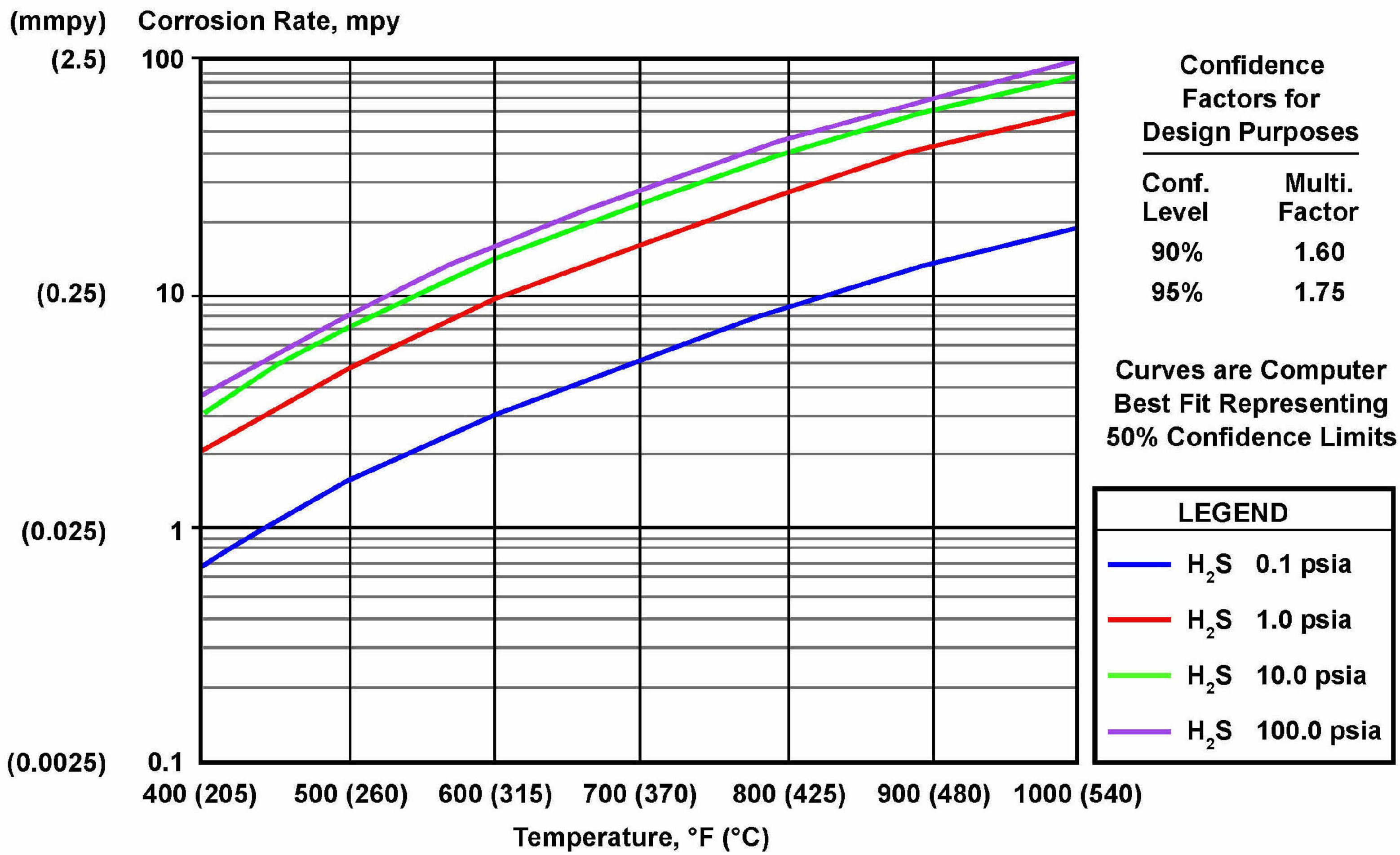


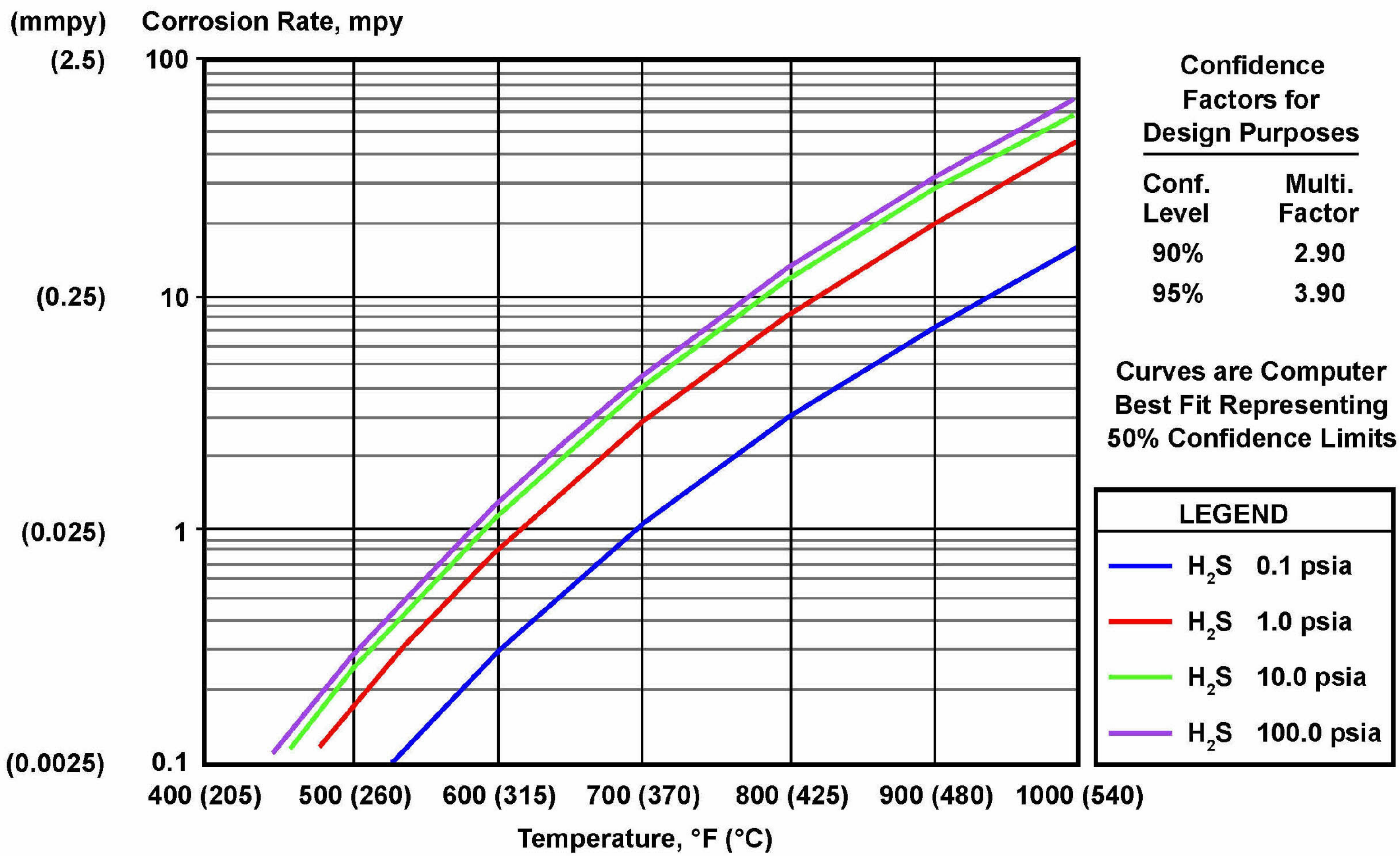
**Figure 2** FCC Fractionator bottoms piping operating at 150 psig (1 MPa) and 650-700°F (340-370°F). (Image courtesy of BP, reproduced courtesy of the American Petroleum Institute).

# Appendix A

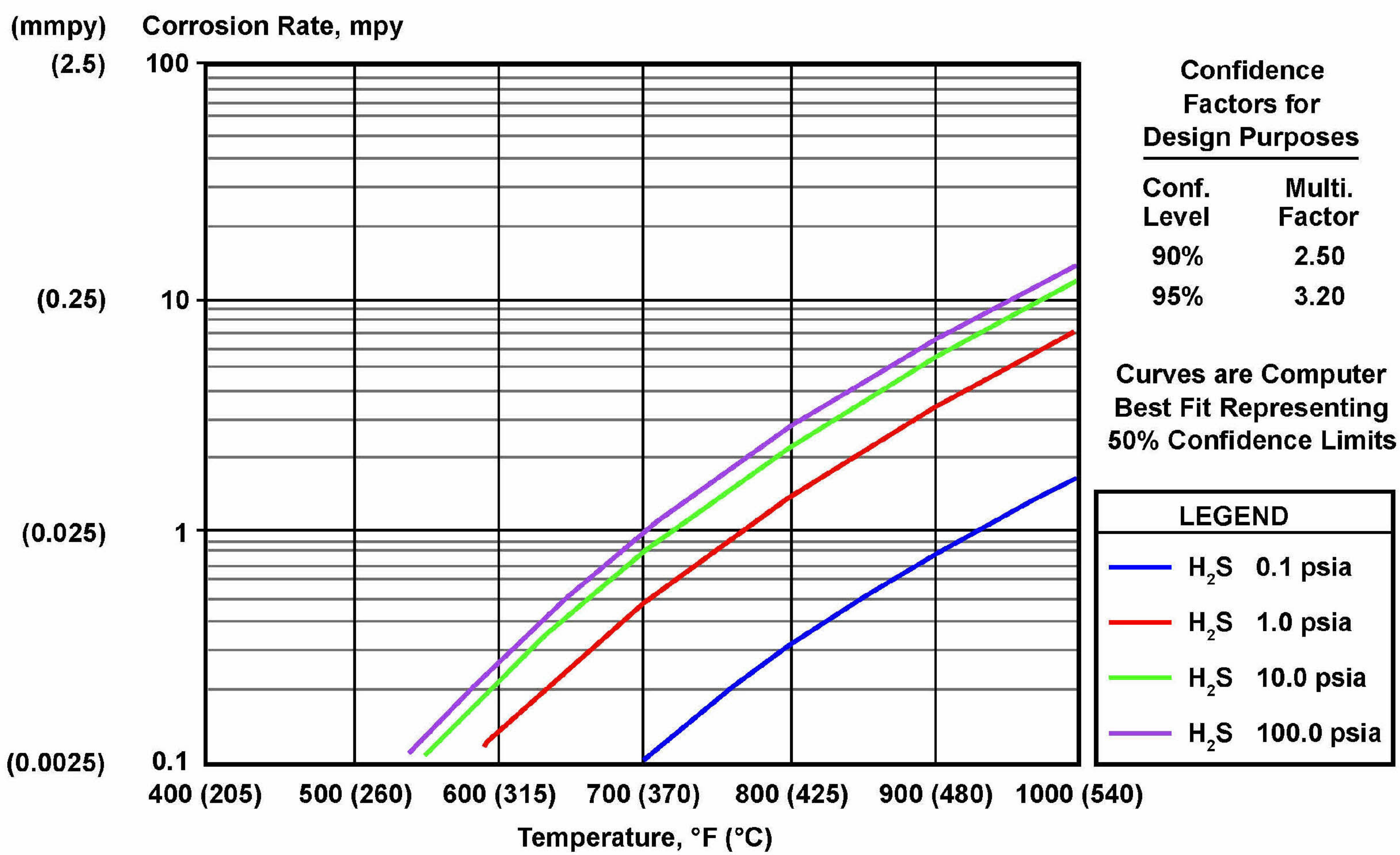
## Chevron $H_2/H_2S$ Corrosion Curves
## and
## Spreadsheet to Calculate Corrosion Rates




$H_2$ - $H_2S$ Corrosion Curves for 0-7 Cr alloys




**$H_2$ - $H_2S$ Corrosion Curves for 12 Cr steels**




$H_2$ - $H_2S$ Corrosion Curves for 18-8 stainless steels

Spreadsheet to calculate $H_2/H_2S$ corrosion rates based on the proprietary Chevron curves (double click to open the spreadsheet and edit values)

H2S concentration and alloy changes on corrosion rates. For additional background information see CRTC report " High Temperature H2 - H2S Corrosion Computer Curve Fitting of Coupon Data" - 11/30/79 - File 16.10.35.

Enter alloy, H2S pp and temp. information below - corrosion rates are automatically calculated in table at right:

| Variable | Enter Value |
|---|---|
| Material - enter "0-7Cr", "12Cr" or "18-8SS" | 18-8SS |
| H2S pp (= mol frac. of H2S X total pressure) | 100 |
| Operating Temperature of Interest (Deg. F) | 700 |

*Note: Must enter material class EXACTLY as it's written within the quotation marks.*

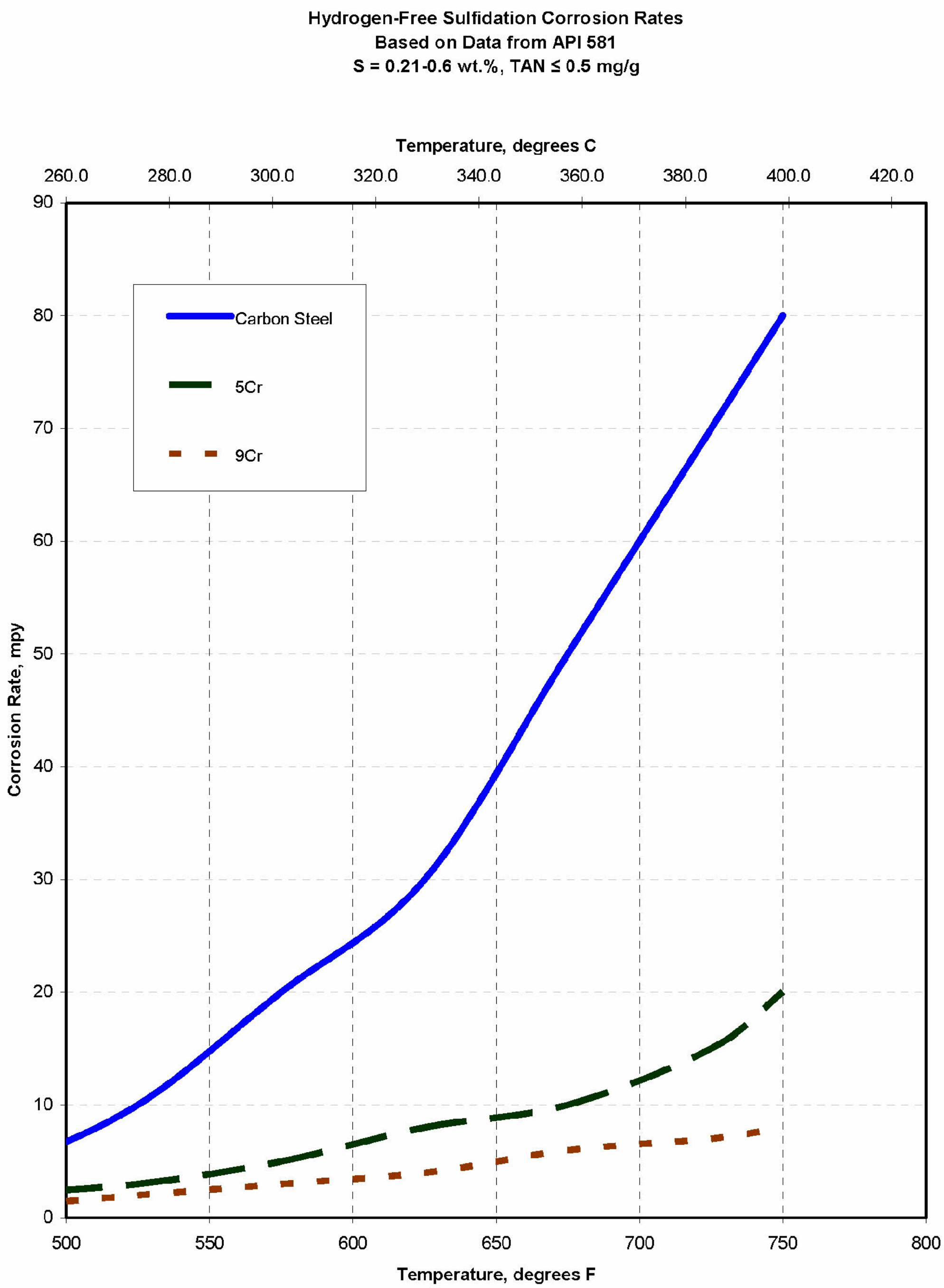
| Calculated Corrosion Rates (mpy) | | |
|---|---|---|
| **Best est. - 50% conf** | **90% conf.** | **95% conf.** |
| 0.8 | 2.0 | 2.5 |

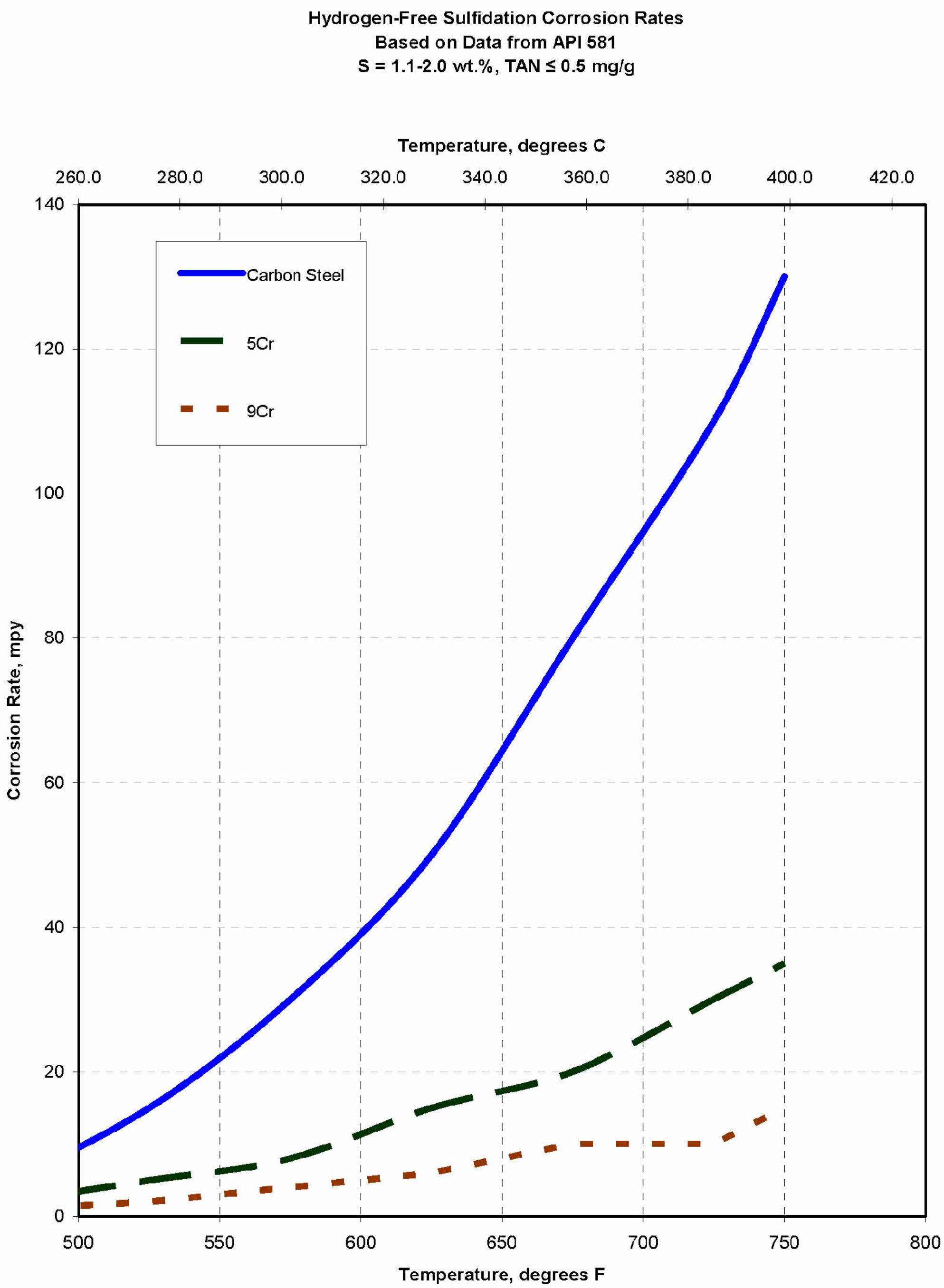
*Note: The 90% confidence level is typically used for design. SS clad construction will typically be recommended when the 90% conf. level corrosion rates exceed 10 mpy.*

| Reference Data *(Do Not alter formulas below)* | Calc. Value |
|---|---|
| Mat'l Constant A (mil sq'd/hr) | 0.29 |
| Material Constant n | 0.45 |
| Material Constant Q (cal/mol) | 34.4 |
| 90% Confidence Factor | 2.5 |
| 95% Confidence Factor | 3.2 |
| Nat. Log k (first term) | 1.471606394 |
| Nat. Log k (second term) | 1.934227708 |
| Natural log k | -0.462621314 |

# Appendix B

## Sulfidation Corrosion Curves for Carbon Steel, 5Cr, and 9Cr Generated from API 581 Tables


Hydrogen-Free Sulfidation Corrosion Rates
Based on Data from API 581
S = 0.21-0.6 wt.%, TAN ≤ 0.5 mg/g
Temperature, degrees C
260.0
280.0
300.0
320.0
340.0
360.0
380.0
400.0
420.0
Carbon Steel
5Cr
9Cr
Corrosion Rate, mpy
0
10
20
30
40
50
60
70
80
90
500
550
600
650
700
750
800
Temperature, degrees F


Hydrogen-Free Sulfidation Corrosion Rates
Based on Data from API 581
S = 1.1-2.0 wt.%, TAN ≤ 0.5 mg/g
Temperature, degrees C
260.0
280.0
300.0
320.0
340.0
360.0
380.0
400.0
420.0
140
120
100
80
60
40
20
0
Carbon Steel
5Cr
9Cr
Corrosion Rate, mpy
500
550
600
650
700
750
800
Temperature, degrees F